

## ORGANIC SCHOTTKY DIODE

### FIELD

This invention relates to a Schottky diode that incorporates a buffer layer between an ohmic contact layer and an organic semiconductor layer.

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### BACKGROUND OF THE INVENTION

The metal-semiconductor junction plays an important role in all solid state devices. A metal-semiconductor junction can be either a rectifying contact or an ohmic contact. Ideally, an ohmic contact displays a linear relationship between current and voltage. A rectifying contact displays a superlinear relationship between current and voltage. In practice, a rectifying contact may be used to create a diode. A diode acts as a sort of electronic valve, allowing a large amount of current to flow in one direction of a circuit, while allowing a negligible amount of current to flow in the opposite direction. A diode requires a certain amount of voltage to be applied across it before significant current will flow. This voltage is referred to as the “forward operating voltage”,  $V_f$ , and is defined as the forward bias required to pass a specified forward current (or current density) through the diode. While a diode generally will not allow significant current flow in the reverse direction, if a large enough reverse bias is applied, the diode will allow significant amounts of current to flow in the reverse direction. This reverse bias is commonly referred to as the breakdown voltage and is defined to be the voltage at which a specified reverse current (or current density) is passed through the diode.

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One type of diode, commonly called the Schottky diode, is made from the junction of a metal and a semiconductor. A typical Schottky diode consists of a semiconductor sandwiched between two different metals. One metal forms an ohmic contact to the semiconductor, while the other metal forms a rectifying contact to the semiconductor.

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Semiconductors utilize electrons and holes as carriers. A semiconductor that has electrons as the majority carrier is usually referred to as an n-type semiconductor, or as having electron-type conductivity. A semiconductor that has holes as the majority carrier is usually referred to as a p-type semiconductor, or as having hole-type conductivity.

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For electron transport in an organic semiconductor, a rectifying contact is formed when the Fermi energy of the metal is lower than the energy of the conduction band edge of the semiconductor. The conduction band edge is also commonly referred to as the

Lowest Unoccupied Molecular Orbital (LUMO) of the semiconductor. An ohmic contact for electron transport in an organic semiconductor is formed when the Fermi energy of the metal is higher than the conduction band edge of the semiconductor. Alternatively, an ohmic contact may be formed by heavily n-type doping the semiconductor adjacent the ohmic contact metal. (See S.M. Sze, Physics of Semiconductor Devices, 1981). The opposite situation applies to hole transport in organic semiconductors. An ohmic contact for hole transport in an organic semiconductor is formed when the Fermi energy of the metal is lower than the energy of the valence band edge, also referred to as the Highest Occupied Molecular Orbital (HOMO), of the semiconductor. An ohmic contact for hole transport may also be formed by heavily p-type doping the semiconductor adjacent the ohmic contact metal. A rectifying contact is formed for hole transport in an organic semiconductor when the Fermi energy of the metal is higher than energy of the valence band edge of the semiconductor.

Traditionally, inorganic silicon and gallium arsenide semiconductors have dominated the semiconductor industry. In recent years, however, there has been an increasing desire to use organic semiconductors as an alternative to the traditional inorganic semiconductors. One organic semiconductor is pentacene, a  $\pi$ -conjugated molecule. In its polycrystalline form, pentacene has relatively high hole mobility parallel to the surface of film for an organic semiconductor. The valence band edge of pentacene is about 4.9 eV below the vacuum level. Therefore, gold, with a work function of 5.1 eV, forms an ohmic contact for holes with pentacene, while aluminum, with a work function of 4.3 eV, creates a rectifying contact for holes with pentacene.

Schottky diodes have been made using organic semiconductors, including pentacene (Y.S Lee, J.H Park, J.S. Choi, Optical Materials, 21, 433-437, (2002)). However, unlike inorganic semiconductors, organic semiconductors are not usually doped in order to achieve their carrier transport properties. Controlled doping to influence the electrical properties of organic transport layers is a new development. Substances like polycrystalline phthalocyananines and amorphous 4,4',4"-tris (N,N-diphenyl-amino) triphenylamine (TDATA) can be doped with the strong organic acceptor tetrafluoro-tetracyanoquinodimethane (F<sub>4</sub>-TCNQ), resulting in conductivity much larger than the undoped material. (M. Pfeffer, A. Beyer, T. Fritz, K. Leo, Appl. Phys. Lett., 73, 729, (1998)).

Organic light-emitting diodes (OLEDs) have received much attention in recent years. Very low operating voltage multi-layered OLEDs have been achieved by combining a thick doped hole transport layer of TDATA with a thin undoped buffer layer of triphenyl-diamine (TPD). This structure resulted in OLEDs with a lower operating voltage and an improved electroluminescent efficiency compared to undoped devices. (X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, K. Leo, Appl. Phys. Lett. **78**, 410-412, (2001)).

Use of doped amorphous materials has also been applied to metal/intrinsic/p-doped (Mip) diodes using 4,4',4"-tris (3-methylphenylphenyl amino) triphenyl-amine (MTDATA) in its intrinsic form, as well as doped with F<sub>4</sub>-TCNQ. Conductivity was shown to increase with increased doping of MTDATA, and both the breakdown voltage and forward voltage of the Mip diode could be increased by thickening the intrinsic layer. (J. Dreschel, M. Pfeiffer, X. Zhou, A. Nollau, K. Leo, Synthetic Metals, **127**, 201-05, (2002)).

A typical organic Schottky diode, such as one made with gold, pentacene and aluminum, exhibits three significant characteristics: (1) it has a low forward voltage in the forward-bias mode; (2) it has a low breakdown voltage in the reverse bias mode; and (3) the device is not robust, and it is easy to get short circuits in practical applications. For certain electronic applications, such as radio frequency identification (RFID) tags, a much higher breakdown voltage is required, while maintaining a relatively low forward voltage. Also, more robust devices that do not get short circuits are also desirable.

## SUMMARY

Briefly, the present invention is an organic Schottky diode that includes a doped buffer layer between the organic semiconductor and the ohmic contact. It has been discovered that adding a doped buffer layer between the ohmic contact and the organic semiconductor greatly increases the magnitude of the breakdown voltage with a relatively small increase in the magnitude of the forward voltage. In addition, the use of a doped buffer layer between the ohmic contact and the organic semiconductor creates a more robust device by preventing spiking of the ohmic contact through the organic semiconductor, thereby increasing the yield of useful devices.

## BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a profile of an organic Schottky diode with a doped buffer layer between the ohmic contact and organic semiconductor.

FIG. 2 is an energy band diagram of an organic Schottky diode with a doped buffer layer between the ohmic contact and the organic semiconductor.

FIG. 3 is a plot of the current-voltage (I-V) relationship for an organic Schottky diode with a buffer layer of MTDATA doped with 5-7% F<sub>4</sub>-TCNQ between the ohmic contact and the organic semiconductor (Example 1).

FIG. 4 is a plot of the I-V relationship for an organic Schottky diode with a buffer layer of MTDATA doped with <5% F<sub>4</sub>-TCNQ between the ohmic contact and the organic semiconductor (Example 2).

FIG. 5 is a plot of the I-V relationship for an organic Schottky diode without a buffer layer between the ohmic contact and the organic semiconductor (Comparative Example A).

The figures may not be drawn to scale. While the above-identified drawing figures set forth embodiments of the invention, other embodiments are also contemplated, as noted in the discussion. In all cases, this disclosure presents the invention by way of representation, and not limitation. It should be understood that numerous other modifications and embodiments that fall within the scope and spirit of the principals of this invention can be devised by those skilled in the art.

## DETAILED DESCRIPTION

Fig. 1 shows organic Schottky diode 10 of the present invention. Diode 10 includes substrate 12, ohmic contact 14, doped buffer layer 16, polycrystalline organic semiconductor layer 18, and Schottky contact 20.

Ohmic contact 14 is placed on substrate 12. Ohmic contact 14 is made of a material that has a suitable work function with respect to doped buffer layer 16. If Schottky diode 10 is to operate by hole transport, then ohmic contact 14 preferably has a large work function suitable for injecting holes into buffer layer 16. If Schottky diode 10 is to operate by electron transport, then ohmic contact 14 preferably has a low work function suitable for injecting electrons into buffer layer 16. For example, gold forms an ohmic contact with many p-type organic semiconductors.

On top of ohmic contact 14 is placed doped buffer layer 16. For example, 4,4',4''-tris (3-methylphenylphenyl amino) triphenylamine (MTDATA) may be used to make

buffer layer 16 if organic semiconductor layer 18 is a p-type material. MTDATA is a stable amorphous glass that functions as a hole transport material for organic light-emitting diodes. Its glass transition temperature is  $\sim 75^{\circ}\text{C}$  and its melting point is  $\sim 203^{\circ}\text{C}$ . Its undoped conductivity is  $10^{-10}$  S/cm at room temperature.

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10 MTDATA may be doped by co-subliming it with acceptor molecules of the fluorinated form of tetracyanoquinodimethane ( $\text{F}_4\text{-TCNQ}$ ). Doping concentrations of 3-20%  $\text{F}_4\text{-TCNQ}$  in MTDATA are effective, with doping concentrations of about 5% to about 10%  $\text{F}_4\text{-TCNQ}$  in MTDATA providing best results.

                  Doped buffer layer 16 may also be made of other materials. If organic  
15 semiconductor 18 is made with a p-type semiconductor, then other p-type doped, amorphous materials may be used to make doped buffer layer 16, including: tetracyanoquinodimethane (TCNQ) doped with tetrathiofulvalene (TTF) (A.R. Brown, D.M. de Leeuw, E.E. Havinga, A. Pomp, Synthetic Metals, **68**, 65-70, (1994)); poly( $\beta'$ -dodecyloxy(- $\alpha, \alpha', -\alpha', \alpha''$ )terthienyl) (polyDOT<sub>3</sub>) doped with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (C.P. Jarrett, R.H.  
20 Friend, A.R. Brown, and D.M. de Leeuw, J. Appl. Phys., **77**, 6289-6294, (1995)); poly(3-hexylthiophene) (PHT) or quinquethiophene (QT) doped with arachidic acid (J. Paloheimo, P. Kulvalainen, H. Stubb, E. Vuorimaa, and P. Yli-Lahti, Appl. Phys. Lett., **56**, 1157-1159, (1990)) ; lutetium and thulium bisphthalocyanines exposed to air to react with  $\text{O}_2$  (G. Guillaud, M. AL Sadoun, M. Maitrot, J. Simon, and M. Bouvet, Chem. Phys. Lett., **167**,  
25 503-506, (1990)) ; or  $\text{C}_{60}$  doped with indium or antimony (K. Hoshimono, S. Fujimori, S. Fujita, and S. Fujita, Jpn. J. Appl. Phys., **32**, L1070-L1073, (1993)). If organic semiconductor 18 is made with an n-type semiconductor, then doped buffer layer 16 must be made of an n-type doped, amorphous material, such as naphthalenetetracarboxylic dianhydride (NTCDA) doped with bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) (A. Nollau, M.  
30 Pfeiffer, T. Fritz, and K. Leo, J. Appl. Phys., **87**, 4340-4343, (2000)) or cationic dye pronin

B chloride (A. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, K. Leo, and S. Machill, Adv. Funct. Mater., 14, 255-260, (2004)) .

Organic semiconductor 18 is placed on top of doped buffer layer 16. The organic semiconductor has a polycrystalline structure and is made of any material that provides suitable semiconducting properties. Pentacene is a desirable organic semiconductor because of its relatively high carrier mobility. However, other p-type organic semiconductors could also be used, including: metal-free phthalocyanine (e.g., H<sub>2</sub>Pc) and metallophthalocyanine (wherein the metal is copper, vanadyl (VO), nickel, iron, lead, zinc, magnesium, or cobalt); fullerene (C<sub>60</sub>) doped with indium or antimony; polyaniline; polypyrrole; poly(p-phenylene); poly(p-phenylenevinylene); substituted pentacene compounds, which are described in Assignee's co-pending application U.S.S.N. 10/256,616, published as U.S. 2003-0105365; bis(2-acenyl)acetylene compounds, which are described in Assignee's co-pending application U.S.S.N. 10/620,027; or acene-thiophene compounds, which are described in Assignee's co-pending application U.S.S.N. 10/641730, all of which are incorporated by reference herein. Organic semiconductor 18 may also be made of an n-type organic semiconductor, including: hexadecahalogenated metallophthalocyanines, such as F<sub>16</sub>CuPc, F<sub>16</sub>ZnPc, F<sub>16</sub>FePc, and F<sub>16</sub>CoPc (Z. Bao, A.J. Lovinger, and J. Brown, J. Am. Chem. Soc., 120, 207-208, (1998)); or N,N'-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C8H) (P.R.L. Malenfant, C.D. Dimitrakopoulos, J. Gelorme, L.L. Kosbar, and T.O. Graham, Appl. Phys. Lett., 80, 2517-2519, (2002)).

Schottky contact 20 is placed on top of organic semiconductor 18. Schottky contact 20 is made of material that has a suitable work function with respect to organic semiconductor 18. If Schottky diode 10 operates by hole transport, then Schottky contact 20 must have a Fermi energy higher than the valence band edge of organic semiconductor layer 18. If Schottky diode 10 operates by electron transport, then Schottky contact 20 must have a Fermi energy less than the conduction band edge of organic semiconductor layer 18. For instance, aluminum forms a Schottky contact with respect to hole transport in pentacene.

In building organic semiconductor diodes, one problem is spiking. No surface is perfectly smooth. When a thin layer of semiconducting material is placed between two layers of metal, the metal may spike through the semiconductor and come into direct contact with the other metal. This creates an undesirable short circuit through the semiconductor.

Buffer layer 16 is made from an amorphous material. As a result, buffer layer 16 smoothes out the rougher surface of ohmic contact 14. Buffer layer 16 also increases the distance between ohmic contact 14 and Schottky contact 20. Using a thicker layer of organic semiconductor 18 would also increase the distance between ohmic contact 14 and Schottky contact 20. However, the thicker undoped organic semiconductor layer would also increase the forward voltage of diode 10, which is undesirable. The addition of buffer layer 16 decreases the probability of spiking, thus making the device more robust, while maintaining a relatively low forward voltage. Buffer layer 16 is at least 1500 Å thick, and it may be as thick as 10,000 Å. Optimal performance is achieved with buffer layer 16 between 2000 Å and 5000 Å.

Fig. 2 shows an energy band diagram for organic Schottky diode 10 in its equilibrium state. The figure includes ohmic contact 14, doped buffer layer 16, organic semiconductor 18, rectifying contact 20, LUMO energy 22, HOMO energy 24 and Fermi energy 26. Holes are injected from ohmic contact 14 to doped buffer layer 16. The holes travel through doped buffer layer 16 into organic semiconductor 18. The holes travel through organic semiconductor 18 to rectifying contact 20. When organic Schottky diode 10 is forwardly biased, the barrier between organic semiconductor 18 and rectifying contact 20 is reduced by the forward bias, allowing the holes to flow freely from organic semiconductor 18 to rectifying contact 20. In contrast, when a reverse bias is applied to organic Schottky diode 10, the barrier between organic semiconductor 18 and rectifying contact 20 prevents the flow of holes in the reverse direction.

### EXAMPLES

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

#### Example 1

Fig. 3 shows a typical I-V curve for an organic Schottky diode that includes a doped buffer layer between the semiconductor layer and the ohmic contact layer. In Fig. 3, the absolute value of current density is plotted along the vertical axis, and bias voltage is plotted along the horizontal axis. This particular diode has an ohmic contact made of 30 Å of titanium and 600 Å of gold, a doped buffer layer made of 3500 Å of MTDATA doped with 5-

7% of F<sub>4</sub>-TCNQ, an organic semiconductor layer made of 3000 Å of pentacene, and a rectifying contact made of 2000 Å of aluminum. A much improved breakdown voltage is observed on the reverse bias side. Even at -50 volts, the leakage current density is still maintained at 10<sup>-5</sup> A/mm<sup>2</sup>.

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#### Example 2

The dopant concentration in doped buffer layer 16 affects both forward voltage and breakdown voltage. Fig. 4 shows an organic Schottky diode that has an ohmic contact made of 20 Å of titanium and 500 Å of gold, a doped buffer layer made of 3200 Å of MTDATA doped with less than 5% of F<sub>4</sub>-TCNQ, an organic semiconductor layer made of 4900 Å of pentacene, and a rectifying contact made of 2000 Å of aluminum. This device has a structure similar to that of the device shown in Fig. 3, except that the doping level of F<sub>4</sub>-TCNQ in the MTDATA is smaller. In Fig. 4, the absolute value of current density is plotted along the vertical axis, and bias voltage is plotted along the horizontal axis. With this lower level of doping, an even better breakdown voltage of more than -60 volts is achieved. However, the forward voltage increases to 15 volts.

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#### Comparative Example A

For comparison, Figure 5 shows an organic Schottky diode made without doped buffer layer 16. This particular diode has an ohmic contact made of 20 Å of titanium and 550 Å of gold, an organic semiconductor layer made of 4900 Å of pentacene, and a rectifying contact made of 2000 Å of aluminum. In Fig. 5, the absolute value of current density is plotted along the vertical axis, and bias voltage is plotted along the horizontal axis.

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Comparing Fig. 3 with Fig. 5, the organic Schottky diode that includes doped buffer layer 16 (Fig. 3) shows an improved breakdown voltage of beyond -50 volts, compared with a breakdown voltage of -36 volts for the traditional Schottky diode (Fig. 5). Yet the diode whose I-V curve is shown in Fig. 3 still exhibits a low forward voltage of about 9 volts.

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#### Examples 3-5

In general, the level of doping will affect both the forward voltage and the breakdown voltage. To increase the breakdown voltage, which is generally desirable, one must also increase the forward voltage, which is generally undesirable. Table 1 summarizes the effect of doping MTDATA with F<sub>4</sub>-TCNQ on the forward voltage and the breakdown voltage.

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Table 1

Example	% of Doping	Thickness of Buffer Layer (Å)	Thickness of Pentacene (Å)	Forward Voltage (volts) @10 <sup>-3</sup> amps/mm <sup>2</sup>	Reverse-bias Current Density
1	5-7%	3500	3000	9.2	~7.5 x 10 <sup>-6</sup> A/mm <sup>2</sup> @ -40V ~1.0 x 10 <sup>-5</sup> A/mm <sup>2</sup> @ -50V
2	Less than 5%	3200	4900	14.8	8.2 x 10 <sup>-7</sup> A/mm <sup>2</sup> @ -60V
3	5%	3000	4000	5-7	~3.5 x 10 <sup>-5</sup> A/mm <sup>2</sup> @ -40V ~8.3 x 10 <sup>-5</sup> A/mm <sup>2</sup> @ -45V
4	14% for the initial 350Å leveling off to 5% for the remaining 2650Å	3000	4830	12.1	~1.1 x 10 <sup>-5</sup> A/mm <sup>2</sup> @ -40V
5	~5% (% fluctuated)	3760	4970	17.5-21	~6 x 10 <sup>-8</sup> A/mm <sup>2</sup> @ -40V ~1.3 x 10 <sup>-6</sup> A/mm <sup>2</sup> @ -60V
A	None	None	4900	5.7	Breakdown occurred at -36V

- 5 Adding a doped buffer layer between the ohmic contact and the semiconductor layer of an organic Schottky diode greatly enhances the breakdown voltage of the device, while still maintaining a forward voltage at a practical level. In addition, the added buffer layer prevents spiking between the ohmic contact and the Schottky contact, thereby creating a more robust device and increasing the yield of useful devices.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention. For example, the whole sequence of the structure above the substrate shown in Fig. 1 may be reversed and may still  
5 achieve the same improved performance.